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TITLE: LITHIUM SECONDARY BATTERY

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ABSTRACT:

PURPOSE: To improve the high-rate discharge characteristic at a low temperature by using a lithium secondary battery added with gamma butyrolactone of a specific range % (volume &) to a mixture of ethylene carbonate and dimethyl carbonate at the specific volume ratio.

CONSTITUTION: The dielectric constant of an electrolyte added and mixed with gamma butyrolactone to a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) at the volume ratio of 1:1 at -20°C is higher than that of the conventional mixture of EC+DMC+DEC (2:2:1). LiCoO₂ having the average grain size of 6μm, acetylene black powder, and polyvinylidene fluoride are mixed, N-methyl pyrrolidone is added into a paste shape, and it is coated with an Al foil to form a positive electrode plate, for example.

Artificial graphite and spherical graphite are mixed, polyvinylidene is mixed, N-methyl pyrrolidone is added, and it is applied to a copper foil to form a negative electrode plate. Both electrode plates are stored in a container, and the electrolyte is injected to obtain a battery having a high-rate discharge characteristic at a low temperature.

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(54) LITHIUM SECONDARY BATTERY

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a lithium secondary battery.

[0002]

[Description of the Prior Art] a lithium secondary battery -- the high voltage -- high energy -- although it was a consistency cell, there was a problem in respect of safety. The lithium secondary battery which used the carbon material for the negative electrode has remarkably high safety as compared with the conventional cell which used the metal lithium for the negative electrode. Since energy density is high, especially the lithium secondary battery using graphite as a carbon material is excellent. However, as for graphite, it turned out that a charge-and-discharge property falls greatly depending on the class of electrolytic solution. That is, the graphite negative electrode was understood that affinity with propylene carbonate (PC) is bad, and ethylene carbonate (EC) is good. However, EC has a problem in the point that the congealing point is high (it is a solid-state at a room temperature).

[0003] As a result of examining the additive on which the congealing point of EC is reduced and neither conductivity nor stability is reduced, what mixed diethyl carbonate (DEC) so that it might become EC:DMC:DEC=2:2:1 (volume ratio) is used for 1:1 mixture (volume ratio) of current, ethylene carbonate, and dimethyl carbonate (DMC).

[0004] DMC reduces the viscosity of the electrolytic solution and is effective in raising low-temperature conductivity. DMC is mixed by EC and 1:1 because the congealing point falls most at this time. If DEC is added, the congealing point will fall further and a low-temperature property will improve.

[0005] However, if the organic electrolytic solution is used for the lithium secondary battery at all, its property fall at low temperature is remarkable, and it is an always important technical problem to improve this property. That is, it is important to raise the electric conductivity in low temperature, such as -20 etc. degrees C. However, don't sacrifice high temperature oxidation stability at this time.

[0006]

[Means for Solving the Problem] This invention solves the aforementioned technical problem using the lithium secondary battery characterized for a gamma butyrolactone by 0.5% or more and carrying out addition 50% or less (volume fraction) into 1:1 (volume ratio) mixture of ethylene carbonate and dimethyl carbonate.

[0007]

[Function] The artificer tried to mix various solvents into 1:1 mixture of EC and DMC, and to improve low-temperature electric conductivity. Consequently, it turned out that the effectiveness which was excellent when the gamma butyrolactone (GBL) was mixed is acquired. However, conductivity was also found by falling on the contrary when the addition of GBL was increased too much. It is thought that GBL is added and electric conductivity will improve because GBL has high solute solubility in order for the congealing point to fall further.

[0008] Moreover, as compared with the conventional DME addition article, the stability in the elevated temperature exceeding 60 degrees C also understood that the GBL addition article excelled more. This is

considered that GBL which has cyclic structure will be because it excels in respect of [DEC / with straight chain structure] stability. In addition, since DMC also has straight chain structure, it is thought that it is inferior in respect of stability, but since other suitable solvents which have the effectiveness of reducing the viscosity of the electrolytic solution cannot be found, for the moment, it cannot but use.

[0009]

[Example] An example is shown below.

[0010] A thing [the conductivity of the conventional EC+DMC+DEC (2:2:1) electrolytic solution / conductivity / -20 degree C / of the electrolytic solution which carried out addition mixing of the gamma butyrolactone (GBL)] is shown in 1:1 (volume ratio) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) at drawing 1. The electrolytic solution which added GBL from 0.5% to 50% so that clearly from drawing shows an EQC or the high conductivity beyond it as compared with the conventional electrolytic solution.

[0011] Next, the lithium secondary battery of this invention was manufactured as follows.

[0012] Mean diameter 6 Micron LiCoO₂ Acetylene black powder and polyvinylidene fluoride were mixed to 86:5:9 (weight ratio), N-methyl pyrrolidone was added, and it was made the shape of a paste, and applied to the aluminium foil whose thickness is 20 microns. For 0.150mm and width of face, 40mm and die length are [the strip-of-paper-like positive-electrode plate 40mm and whose die length it cuts after drying and rolling this out, and 0.150mm and width of face are 28mm for thickness, and / thickness] 300mm. The band-like positive-electrode plate was made as an experiment.

[0013] Next, they are artificial graphite with a mean particle diameter of 25 microns and 20-micron spherical graphite at a weight ratio 3:1 The mixed graphite mixture and polyvinylidene fluoride were mixed to 86:14 (weight ratio), N-methyl pyrrolidone was added, and it was made the shape of a paste, and applied to the copper foil whose thickness is 18 microns. It cuts, after drying and rolling this out, and for 0.110mm and width of face, 41mm and die length are [thickness] 430mm. The band-like negative-electrode plate was made as an experiment.

[0014] The strip-of-paper-like positive-electrode plate was used as the winding core, and it wound with the band-like negative-electrode plate through the fine porosity film polyethylene separator whose thickness is 25 microns, and it continued further, the band-like positive-electrode plate was wound, and the winding side made the ellipse-like cell generation-of-electrical-energy element as an experiment.

[0015] 70-micron PP film is pasted up for the above-mentioned generation-of-electrical-energy element on an inside, and it is 8 to external surface. It sealed on the square shape container and container lid with a thickness of 0.22mm made from a steel plate which gave the paint film of a micron, and the positive-electrode plate and the negative-electrode plate were electrically connected to the rivet terminal made from stainless steel (two pieces) prepared in the container lid, respectively. As for the rivet terminal, the insulation and the airtight are maintained by the gasket made from a methyl pentene copolymer (TPX). Moreover, airtight obturation of a container lid and the container is carried out by double winding up obturation.

[0016] The lithium secondary battery (A) of this invention which poured the EC+DMC+GBL (40:40:10) electrolytic solution in the above-mentioned cell, and cell (a) for the comparison which poured in EC+DMC+DEC (40:40:20) were made as an experiment. these cells -- ordinary temperature -- 200mA up to 4.1V -- charging -- 500mA 2.75V up to -- it discharged. Then, charge and discharge were similarly carried out by -20 **. The comparison of the discharge capacity at this time is shown in Table 1.

[0017]

[Table 1]

	25°C	-20°C
電池(A)	800mAh	300mAh
電池(ア)	600mAh	50mAh

The cell of this invention has few falls of the discharge capacity in low temperature as compared with

the conventional cell so that clearly from Table 1.

[0018]

[Effect of the Invention] The lithium secondary battery in which the high-rate-discharge property at the time of low temperature was excellent with this invention can be obtained.

[Translation done.]